Pulsed 1064 nm Nd-YAG Laser Deposition of Titanium on Silicon in a Nitrogen Enviroment

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ABSTRACT

Pulsed laser deposition (PLD) technique was demonstrated for the deposition of titanium nitride (TiN) thin films on Si (100) substrates. A 1064 nm pulsed Nd-YAG laser is focused on a titanium (99.5%) target in a nitrogen environment to generate the atomic flux needed for the film deposition. Spectroscopic analysis of the plasma emission indicates the presence of atomic titanium and nitrogen, which are the precursors of TiN. Images of the films grown at different laser pulse energies show an increase in the number and size of deposited droplets and clusters with increasing laser pulse energy. A decrease in cluster and droplet size is also observed, with an increase in substrate temperature. EDS data show an increase in the titanium peak relative to the silicon as the ambient nitrogen pressure is decreased. An increase in deposition time was found to result in large clusters and irregularly shaped structures on the substrate. Post-deposition annealing of the samples enhanced the crystallinity of the film.

Keywords: laser deposition, titanium nitride, laser-induced plasma.

INTRODUCTION

Pulsed laser deposition (PLD) is an emerging technology for producing high quality thin films of virtually any material from pure elements and simple to complex multicomponent compounds. It has been used to fabricate films of monocrystalline epitaxial molybdenum (Malikov & Mikhailov, 1997), epitaxial $Al_xGa_{1-x}N$ (Huan & Harris Jr., 1998), 4-cyano-4'-pentybiphenyl (5CB) liquid crystal (Gonzalo et al., 1997), optically active Er-Yb doped glass (Serna et al., 1998), and highly crystalline superconducting $YBa_2Cu_3O_7$ (Wong et al., 1997).

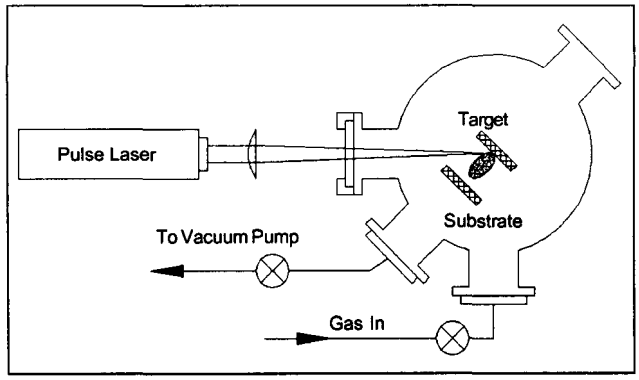

Fig. 1. Schematic diagram of the Pulsed Laser Deposition (PLD) System

Conceptually and experimentally, PLD is one of the simplest and most flexible among the thin film growth laser and laser beam handling optics. The chamber is provided with optical windows, target and substrate mounts. To generate the atomic or molecular flux needed in the deposition process, the laser output beam is

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focused with a lens to sufficient high intensity to excite, vaporize, and ablate a target. The process forms a high temperature transient plasma consisting of electrons, ions, and excited species of atoms and molecules. The ejected materials expand in the forward direction and normal to the target. The film is grown by placing a substrate along the path of the expanding plasma and allowing the ejected materials to condense on it. Oxygen, nitrogen, or any other gas can be introduced into the chamber to mediate with the energetic species in the plume or react with the ablated materials.

Compared to conventional thin film deposition technique such as evaporation, sputtering, chemical vapor deposition, and molecular beam epitaxy, PLD has several advantages. It offers greater flexibility and freedom in the design of the deposition system. The energy source is externally located, allowing significant decoupling of deposition parameters. Energy delivery to the target can be easily achieved since laser beams are much easier to handle and transport than electrons or ions. Because of this, materials with high melting point can easily be fabricated. The inherent pulsed nature of the laser leads to a high controllability of the deposition thickness. In PLD, the predominant amount of the evaporated material is forward directed and can be collected with a high degree of efficiency, resulting in a much improved target lifetime. These make the process inherently clean since the plasma generated does not come in contact with the surfaces inside the chamber eliminating the probability of film contamination. Laser induced expulsion preserves the stoichiometry of the target in its transfer to the substrate, making it easier to deposit a complex multielement material. Fabrication of multilayer film is straightforward, with rapid substitution of target in the path of the laser beam. Lastly, PLD also allows deposition in a high partial (mtorr) pressure environment. Introduction of reactive gas to provide the correct abundance of volatile elements will be easily achievable.

However, PLD also has its shortcomings. During the laser interaction with the target, the rapid heating and surface evaporation of the target causes superheating of a subsurface layer that leads to explosive evaporation. Molten globules, micron and submicron particles are ejected and deposited on the substrate. This splashing effect is detrimental to the growth of a uniform film. Several schemes have been proposed to reduce or eliminate the particulates, such as the use of mechanical filters, target conditioning, and reduction of pulse laser energy to value just above the ablation threshold.

Titanium nitride (TiNx, [N]/[Ti] $\cong$ 1) is an important technological material known for its exceptional physical, electrical, and chemical characteristics. Its notable properties are: (1) chemically stable, highly inert, non-toxic, dense, and non-porous; (2) excellent abrasion, corrosion and chemical resistance; (3) low and stable sheet and contact resistance; (4) extremely high thermal stability with a melting point of 2950°C, allowing it to be considered as a refractory material; and (5) ultra hard material - harder than carbide or chrome and among the highest after diamond. Titanium nitride is widely used in commercial and industrial applications as a non-stick, anti-galling, hard and corrosion resistant coating. It can be applied to most metals, ceramics, and plastics to form a layer with a strong bond to the base material that will not blister, flake, or chip.

Recently, titanium nitride has gained much interest in the different areas of silicon device technology as a conductor in metal-base transistors, interconnection in three-dimensional integrated circuits, and as a rectifying, ohmic and schottky barrier contacts (Mihailescu et al., 1993; Chowdhury et al., 1994; Willmot et al., 1997). The most prospective use of titanium nitride is as diffusion barrier in the metallization scheme of very large scale integrated microelectronics. It is capable of resisting silicon interdiffusion with metal layers at temperature of up to 600°C. Titanium nitride also has good etch-stop capability.

In this communication, we report the fabrication of titanium nitride thin film on silicon substrates through PLD. A pulsed Nd-YAG laser is used to ablate a titanium target in a nitrogen environment to deposit a TiN film on silicon. The study includes an investigation on the effects of different deposition parameters on the film quality.

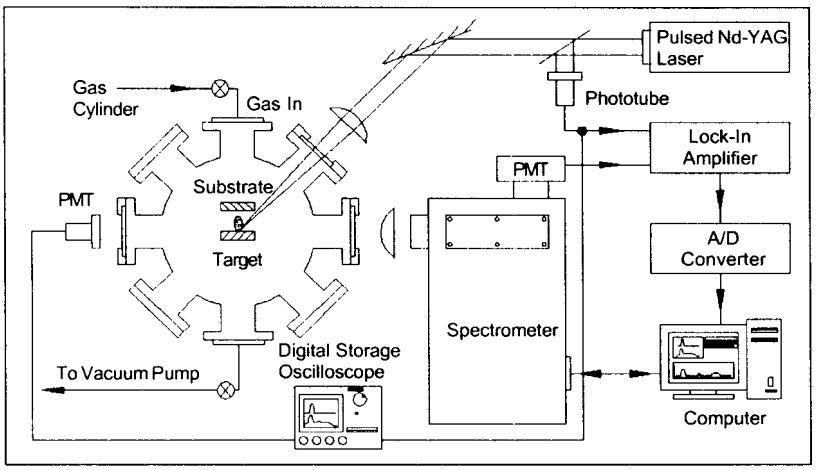

Fig. 2. Schematic diagram of the experimental setup

EXPERIMENTAL SETUP AND METHOLOGY

A schematic diagram of the experimental setup is shown in Fig. 2. The excitation source is a flash lamp pumped Nd-YAG laser (Spectra Physics GCR-230-10) with an output wavelength of 1064 nm. A phototube (Hamamatsu R1328U-01) and a 500 MHz digital storage oscilloscope monitor the laser output. The vacuum chamber is evacuated to a base pressure of 8 x 10^{-3} mbar by a mechanical pump. A gas inlet allows the introduction of ultra high purity nitrogen into the chamber. A titanium disk of 99.5% purity with a dimension of 1-1/2" diameter and 1/4" thickness is placed on the target mount. The pulsed laser output beam is focused on the titanium target with a 50 cm quartz lens to approximately 2 mm spot size. The silicon substrates are cut to a size of about 5 mm square from a 4" wafer oriented in the (100) plane. Before mounting on the holder, it is cleaned to remove grease, dirt, and other contaminants. Using an ultrasonic cleaner, the substrate was soaked in a solution of 10% hydrogen fluoride, followed by reagent grade trichloroethylene, acetone and methanol for about 5 minutes in each solvent. After degreasing, the substrate is blown dry with nitrogen gas.

The plasma generated by the laser interaction with the titanium target in the nitrogen environment is spectroscopically analyzed to determine its composition. The plasma optical emission is collected by a 30 cm lens into the entrance slit of a computer controlled 1-meter monochromator (SPEX 1000M) with a GaAs photomultiplier tube (Hamamatsu R943-02) and a 1200 grooves/mm grating. The signal from the detector is processed by a lock-in amplifier (SRS SR830), an analog to digital converter and displayed on a computer. The lock-in amplifier is triggered by the signal from the phototube. A photomultiplier tube (Hamamatsu R212P) and an oscilloscope monitors the temporal behavior of the plasma.

To characterize the film quality, optical microscopy and scanning electron microscopy (SEM) are used to provide information on surface morphology. Also, the composition of the films is studied with an electron dispersive x-ray spectroscopy (EDS). The presence of titanium nitride is verified with X-ray diffraction (XRD).

The film is deposited with the following parameters:

target to substrate distance: 15 mm
nitrogen background pressure: 9 x 10^{-3} mbar to 1.5 mbar
deposition time: 30 min to 90 min
substrate temperature : 25°C to 400°C
laser excitation energy: 150 to 460 mJ at 10 Hz pulse repetition rate and pulse duration of 30 ns (FWHM)

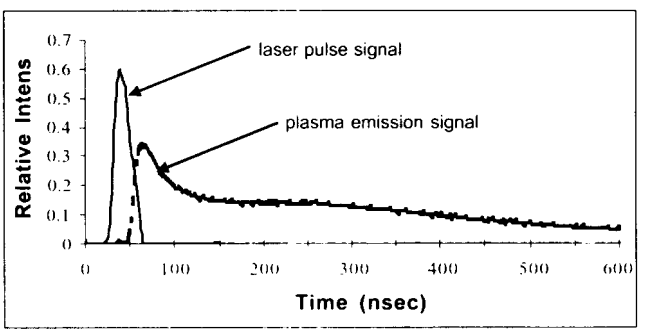

Fig. 3. Temporal behavior of the incident laser pulse and the plasma emission

RESULTS AND DISCUSSIONS

A typical temporal profile of the laser pulse and the plasma emission are shown in Fig. 3. The plasma ignites approximately 10 ns after the laser pulse and slowly decays. Fig. 4 shows the optical emission spectrum of the laser-produced plasma over the range of 5000 to 6000 Å. The data is obtained by scanning the spectrometer at an increment of 1.0 angstrom and slit width of 500 micrometer. Fig. 4a shows the optical emission spectrum of the laser produced plasma. Fig. 4b shows sections of the spectrum corresponding to some of the discrete titanium and atomic nitrogen emission lines. These atomic species form the precursor of the film. Titanium was generated by the laser-target interaction, while collision processes in the plasma produced the atomic nitrogen.

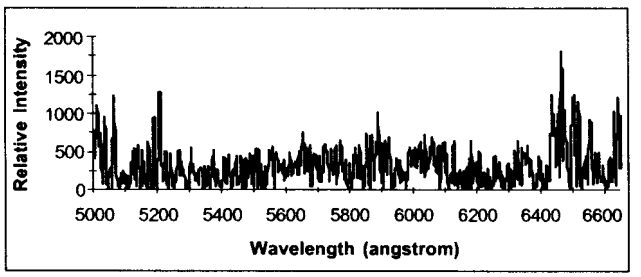

Fig. 4a. Optical emission spectrum of the laser produced plasma

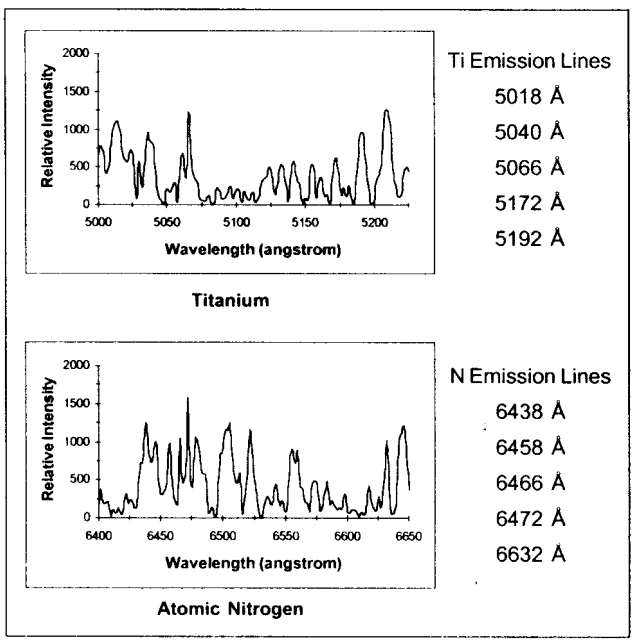

Fig. 4b. Optical emission spectrum of the laser-produced plasma and the observed titanium and atomic nitrogen emission lines

The films deposited at $9x10^{-3}$ mbar nitrogen pressure are observed to have the characteristic gold color of TiN. At higher pressures, the films have a grayish color. A comparison of the EDS data Fig. 5(a) and 5(b) shows a significant decrease in the titanium peak with respect to the silicon peak at higher nitrogen pressure. The increase in pressure reduces the mean free path of the ejected materials. This lessens the number of energetic particles reaching the substrate thereby lowering the thin film growth rate. Based on these data, the optimum nitrogen pressure for the growth of TiN films is $9x10^{-3}$ mbar. Optical microscopy shows that the cluster and droplet size increases with the incident laser energy (Figs. 6 (a) and 6 (b)). This behavior is due to splashing commonly observed at higher laser intensity (Herman et al., 1995). This sets the optimum laser energy per pulse at 150 mJ.

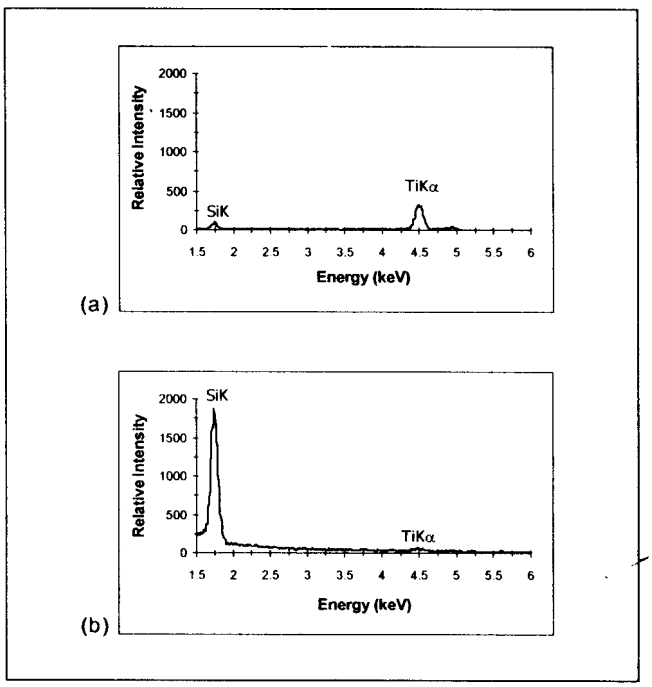

Fig. 5. EDS data of the films deposited at (a) $9x10^{-3}$ mbar and (b) $7x10^{-1}$ mbar N_2 pressure, 200°C substrate temperature for 60 minutes and 150 mJ laser pulse energy

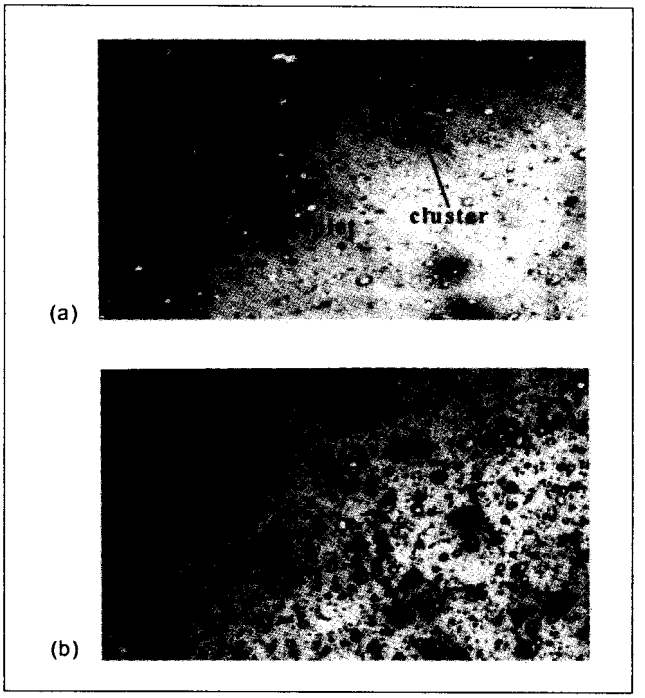

Fig. 6. Optical microscope image (100x) of the films deposited at (a) 150 mJ and (b) 460 mJ laser pulse energy for 60 minutes, 200°C substrate temperature and $9x10^{-3}$ mbar N_2 pressure

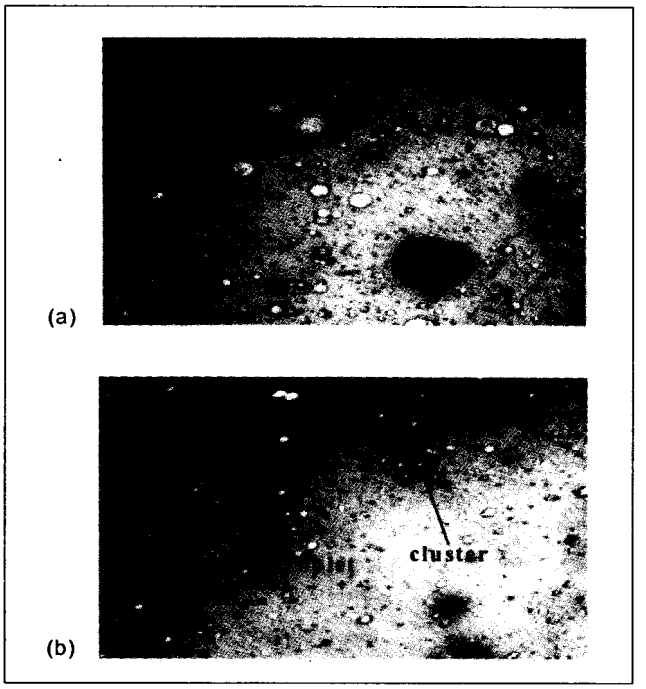

Fig. 7. Optical microscope images (100x) of thin films deposited at (a) 25°C and (b) 400°C substrate temperature for 60 minutes, 150 mJ laser pulse energy and $9x10^{-3}$ mbar N_2 pressure.

Dependence of film uniformity on deposition time and substrate temperature was investigated. Fig. 7 shows the optical microscopy image of films deposited at 25°C (Fig. 7a) and 400°C (Fig. 7b). A higher substrate temperature increases the mobility of diffusing species, improving the uniformity of the deposited film. SEM images of the films deposited for 30 mins (Fig. 8a) and 90 mins (Fig. 8b) is shown at Figs. 8(a) and 8 (b), respectively. Formation of irregularly shaped structures is observed with an increase in deposition time.

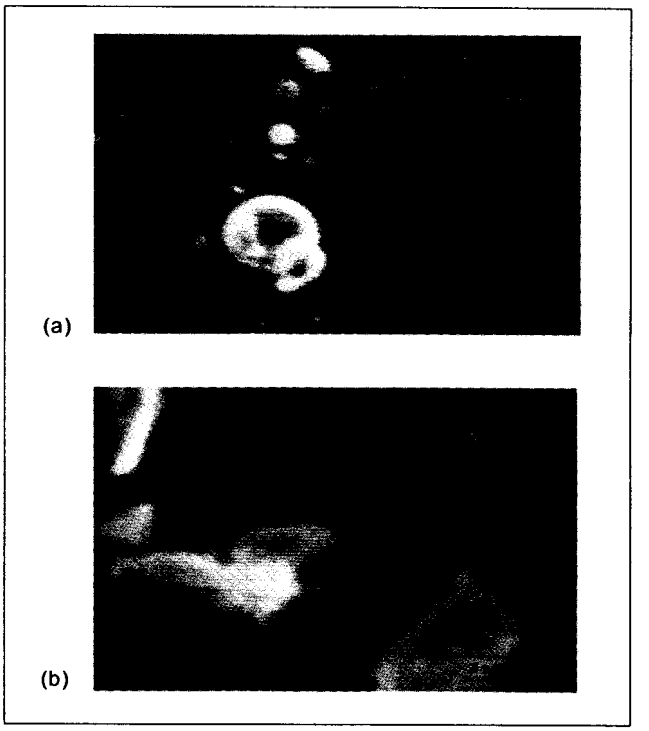

Fig. 8. SEM images (3500x) of the films deposited for (a) 30 minutes and (b) 90 minutes at 150 mJ laser pulse energy, 200°C substrate temperature and $9x\ 10^{-3}$ mbar N_2 pressure

XRD data obtained yielded a negative result, indicating the amorphous nature of the deposited film. The sample deposited at 200°C is annealed at a temperature of 700°C for 6 hours in 1.2×10^{-2} mbar nitrogen pressure. Fig. 9 shows the XRD plot of the film after annealing. The $2\theta = 42.69^{\circ}$ diffraction line corresponds to TiN (200). Peaks due to the diffraction of other crystal planes are not observed.

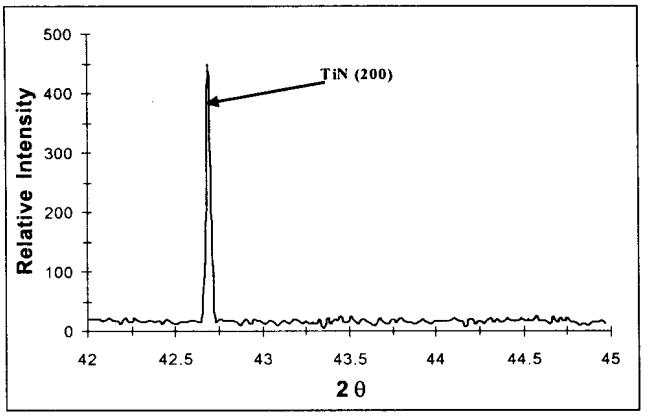

Fig. 9. XRD pattern of the thin film deposited at 200°C substrate temperature after annealing at 700°C for 6 hours.

CONCLUSIONS

Deposition of TiN thin films on silicon is done using a pulsed Nd-YAG laser operating at 1064 nm to excite, vaporize, and ablate a titanium target in a nitrogen environment. The optimum TiN thin film growth parameters of the PLD setup are determined.

At present, we are investigating the use of a shorter laser wavelength to deposit TiN on silicon to attain a more uniform film. Also, to avoid the need of post deposition annealing to produce crystalline titanium nitride films, the deposition will be made at a much higher substrate temperature. Another parameter that requires further investigation is the deposition pressure. In our present work, the optimum deposition pressure is found to be at the base pressure of the chamber. Other areas of research include a study on the exact mechanism of the TiN formation.

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